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## COMPUTATIONAL STUDIES OF ENERGETIC NITRAMINE

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<p>This final report summarizes our computational investigations of energetic materials carried out over a six-year period. It is divided into seven main sections, describing the major themes of this project. First, factors important in designing molecules with high specific impulse values and in determining the sensitivities of energetic systems are discussed, followed by a review of our analyses of reaction energetics (carried out primarily using a local density functional approach). Next, studies aimed at providing insight into possible synthetic routes are summarized, followed by a section on fundamental molecular properties of nitramines. Surface electrostatic potentials of the four known CL-20 polymorphs show significant differences in their tendencies for intermolecular interactions. We have calculated structures and reactive properties for a variety of new energetic materials, including heterocyclic, ionic, mesoionic and zwitterionic systems. We have shown that correlations exist between key calculated properties [the electrostatic potential <math>V(r)</math> and the average local ionization energy <math>\bar{I}(r)</math>] and a number of experimentally-based indices of reactivity.</p>					
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## ONR 6-YEAR REPORT

### SUMMARY AND DISCUSSION OF RESULTS

#### I. Properties Related to Propellant and Explosive Performance

##### A. Specific Impulse

We have developed a procedure for estimating the relative specific impulse ( $I_s$ ) values of monopropellants [1]. This technique assumes that the combustion products are limited to CO, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub> and HF. Except for fluorine-containing systems, the relative  $I_s$  values calculated with this procedure follow in general the same pattern as those obtained using the Naval Weapons Center program [2]. Using both of these methods, we have computed specific impulse values for over sixty compounds, complementing the Navy's synthetic and developmental efforts, e.g. by Dr. J. H. Boyer (UNO) and at the Naval Weapons Center. Using the NWC program, we have also computed specific impulses for several oxidizer/binder mixtures at four different chamber pressures. For the particular binder chosen, a polyethylene derivative, the specific impulse of the mixture was found to be slightly greater (1% - 3%) than for the oxidizer alone.

In the course of our work with specific impulse calculations, we have found that the relative specific impulse is not highly sensitive to the method used for obtaining the heat of formation [2]. For example, the trends in  $I_s$  are in general the same using heats of formation computed with the semiempirical AM1 procedure alone as when they are corrected for crystal effects.

In designing molecules to have high specific impulse values and thus to merit consideration as monopropellants, it is generally desirable to try to satisfy two key criteria: (a) combustion should lead to light gaseous products, so as to maximize the number of moles of gases produced per unit weight of propellant, and (b) the compound should have a large positive heat of formation (on a weight basis), since this results in a high combustion temperature. We have demonstrated the importance of these two factors through both a rationalization based on simplified kinetic theory and a comparative analysis of our calculated relative  $I_s$  values for a large number of molecules [2]. To achieve significant improvement over HMX in specific impulse, it seems necessary to combine molecular features that will lead to both of the consequences (a) and (b). The presence of strain and aza nitrogens favors a high heat of formation, while the inclusion of some hydrogens and fluorines results in light gases (H<sub>2</sub>O and HF) being formed as combustion products.

##### B. Sensitivity

For groups of nitramines and nitroaliphatics, taken separately, we have shown that shock sensitivity is related to the strengths of all of the N-NO<sub>2</sub> and/or C-NO<sub>2</sub> bonds in the molecule, taken in conjunction with its overall size [3-5]. The reciprocals of bond lengths are used as

measures of bond strengths, while molecular weight is taken as the indicator of molecular size. Thus sensitivity  $\sim (n/M)R_{ave}$ , where  $n$  is the number of N-NO<sub>2</sub> or C-NO<sub>2</sub> linkages, having an average N-N or C-N distance of  $R_{ave}$ , and  $M$  is the molecular weight. This work was done in collaboration with Dr. H. Adolph (Naval Surface Weapons Center).

The success of this relationship between shock sensitivity, molecular size and the number and strengths of all N-NO<sub>2</sub> and/or C-NO<sub>2</sub> linkages in groups of nitramines and nitroaliphatics prompted us to investigate whether the same approach could be extended to nitroaromatics. However we found a distinct lack of correlation between impact sensitivity and  $(n/M)R_{ave}$  for a group of eighteen nitroaromatics. For these, we have found instead that a relationship exists between impact/shock sensitivity and a parameter related to the instability of an individual C-NO<sub>2</sub> linkage in the molecule [4].

In connection with our overall objective of understanding factors affecting the sensitivities of energetic compounds, we have analyzed in detail the increase in thermal stability that is observed to accompany the replacement of C(NO<sub>2</sub>)<sub>3</sub> by CF(NO<sub>2</sub>)<sub>2</sub>, and concluded that this is due to the partial relief of the crowding of the three nitro groups together on the same carbon [6]. Further, because nitroaromatics with OH substituents are found to be more sensitive than anticipated, we examined the extent to which the interaction of the OH group with the aromatic ring is affected when the former is rotated from its equilibrium position, as can happen in crystals. We found, in both phenol and *p*-nitrophenol, that rotation has only a very small effect upon the conjugation between the OH and the ring [7]. From the results of a later computational analysis, we have suggested that the high sensitivities of hydroxynitroaromatics may be due to the formation of small quantities of unstable nitronic acid tautomers [4].

Although there seems to be little likelihood of establishing a universal structure-sensitivity relationship covering all types of energetic materials, considerable progress has been made in understanding factors which influence sensitivity within separate categories of compounds [4]. Molecules which do not fit the existing correlations suggest starting points for further investigations aimed at elucidating the basis for their exceptional behavior, as in the case of the hydroxynitroaromatics, for example.

## II. Reaction Energetics

We have increasingly used local density functional (LDF) theory in addition to *ab initio* procedures to calculate the energetics associated with chemical processes, including decomposition, dissociation and rearrangement reactions. The established advantages of this approach are that it makes much smaller demands upon computer resources (CPU time and disk space) than do *ab initio* methods, yet does take account of electronic correlation. Thus it is feasible to treat much larger systems than can be handled *ab initio*. In several exploratory studies, we

found that the LDF approach yields activation barriers that are comparable in accuracy to many-body post-Hartree-Fock techniques. Dissociation energies have been a problem, since LDF theory tends to overestimate them, but we have developed a means for overcoming this [8,9]; we showed that there are excellent correlations between the non-local corrections to the energy and the number of electrons, within isonuclear series.

The reactions for which we have now computed the energetics (activation barriers, dissociation energies, etc.) include:

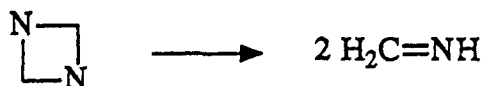
(a) A series of seven small-molecule isomerizations [10]:



(b) Dissociation of the C-H bond in acetylene [11]:



(c) Dissociation of 1,3-diazacyclobutane [12,13]:



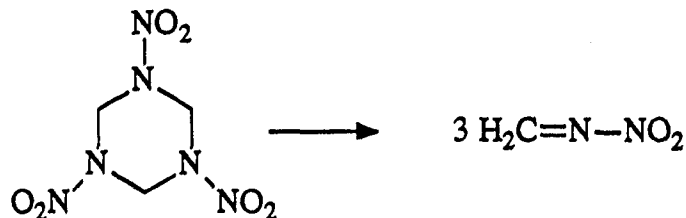
(d) Dissociation of 1,3-dinitro-1,3-diazacyclobutane [12,13]:



(e) Dissociation of 1,3,5-triazacyclohexane [14]:



(f) Dissociation of RDX [14]:



(g) A series of six isomerizations to strained systems [9]; e.g.



### III. Precursors and Preparative Routes in Synthesis

#### A. Substituted Acetylenes as Precursors in Synthesis

In view of the considerable interest in substituted acetylenes,  $R-C\equiv C-R'$ , as potential precursors in a variety of useful syntheses, it is important to understand how their reactive properties are affected by the natures of R and R'. With this objective, we carried out a computational analysis of a group of mono- and disubstituted acetylenes [15]. The substituents included the CH<sub>3</sub>, NO, NO<sub>2</sub> and NH<sub>2</sub> groups. We focused in particular upon relative bond strengths and molecular electrostatic potentials; the latter property is well established as a guide to the reactive behavior of molecules.

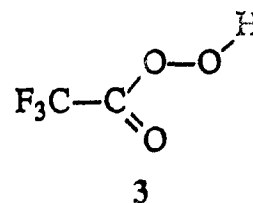
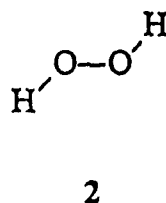
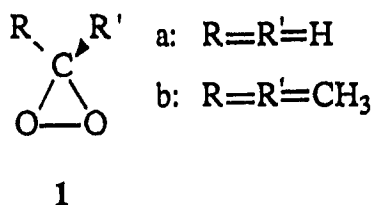
Looking first at the effects of various substituents upon the  $C\equiv C$  bond, we found that the presence of NO<sub>2</sub>, in itself, strengthens this bond, while NO substitution weakens it. A key observation, however, is that the combination of NO<sub>2</sub> and NH<sub>2</sub>, a strong electron donor, has an overall weakening effect (relative to acetylene). It is also of interest that while the C-NO<sub>2</sub> bonds are stronger than the C-NO, the former become weaker in going from mono- to dinitroacetylene, whereas the latter are stronger in dinitrosoacetylene than in the singly substituted derivative.

Proceeding to the molecular electrostatic potentials, a general result is that the strong negative potential associated with the triple bond of acetylene is entirely eliminated by the introduction of even one NO<sub>2</sub>. This is fully consistent with previous observations of the effect of this group, and indicates a diminished susceptibility of the  $C\equiv C$  bond toward electrophilic attack. The NO group has a lesser influence upon the triple bond potential, but in the dinitroso derivative, the latter is again completely positive.

Other significant features of these molecules include buildups of positive potential that are found above the C-NO<sub>2</sub> bond regions. These are believed to indicate the possibility of the C-NO<sub>2</sub> bond serving as an initial site for nucleophilic attack. Indeed, some nitroacetylenes have been observed to be very reactive toward nucleophiles, as has been reported, for example, by R. J. Schmitt and C. D. Bedford (SRI International). Another point of interest is the non-planarity of dinitro and dinitroso- acetylene. In these molecules, the two substituents are found to be in perpendicular planes, presumably to allow each to conjugate individually with one of the  $C\equiv C$   $\pi$  bonds.

## B. Reactive Properties of Dioxirane and Some Peroxides

Dioxiranes, **1**, are effective oxygen atom transfer agents, and they are also intermediates in some reactions of peroxy compounds. In view of these important roles in oxidation processes, we sought a better understanding of how the structure and electronic distribution of dioxirane, **1a**, determine its properties and reactive behavior. Because of the formal similarity between the O—O



bonds in dioxiranes and in peroxides, we included hydrogen peroxide, **2**, and peroxytrifluoroacetic acid, **3**, in our study. The latter is an excellent oxidizing agent, which converts aromatic amines to the nitro derivatives in high yields.

We carried out a computational analysis of the structures and properties of **1a**, **2** and **3**, focusing upon molecular electrostatic potentials, bond deviation indices and relative bond strengths [16]. We find a rather limited sensitivity of the peroxide OOH group to the remainder of the molecule. The structural parameters, the O—O bond deviation index, and the relative bond strengths of both the O—O and O—H bonds are essentially unchanged by either rotation around the O—O bond in  $H_2O_2$  or the presence of the electron-withdrawing  $CF_3C(O)$  group in **3**. The latter does, however, significantly affect the electrostatic potential; the negative regions associated with the peroxide oxygens become weaker, especially the one nearer to the substituent. Thus substantial polarity is introduced into the O—O bond of **3**, which promotes the heterolytic rupture that is believed to be involved in its oxidizing mechanism.

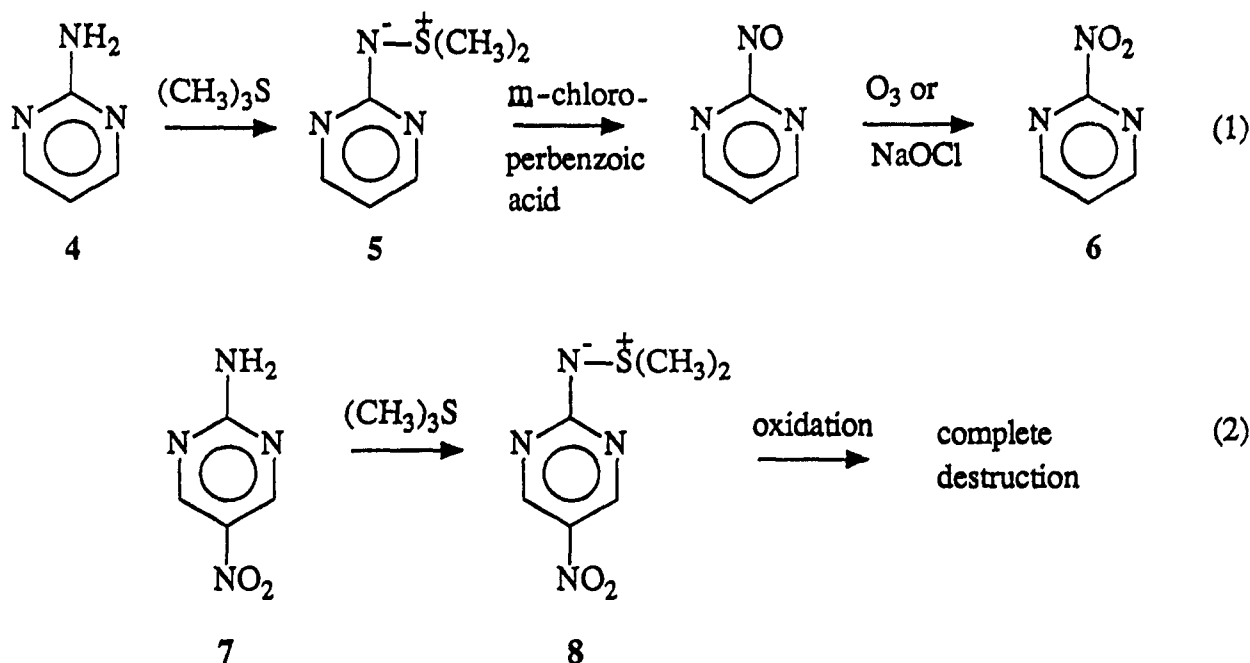
We find the O—O bond in dioxirane (**1a**) to be qualitatively different from those in **2** and **3**. In dioxirane it is considerably strained, and consequently weaker than in **2** and **3**. The C—O bonds are also weakened by strain. The highly reactive nature of dioxirane is thus readily understandable.

## C. Sulfilimine Route to Nitroheterocycles

It has been suggested that the exocyclic  $-NH_2$  groups on heterocyclic amines could be oxidized to  $NO_2$  by proceeding through sulfilimine intermediates, in which the negative character of the exocyclic nitrogen is increased and it is thus made more susceptible to electrophilic attack by the oxidizing agent. This does indeed occur in the case of 2-aminopyrimidine, **4**, which has been found to produce 2-nitropyrimidine, **6**, in 33% yield, as shown in reaction (1).

In order to better understand how the formation of the sulfilimine **5** facilitates the oxidation of **4**, we carried out a detailed computational analysis of both systems [17]. We also investigated a

case in which this procedure fails; reaction (2), which starts with 2-amino-5-nitropyrimidine, 7, leads to the destruction of the heterocyclic system. Our approach involved calculating the optimized geometries of 4, 5, 7 and 8, and then their electrostatic potentials.



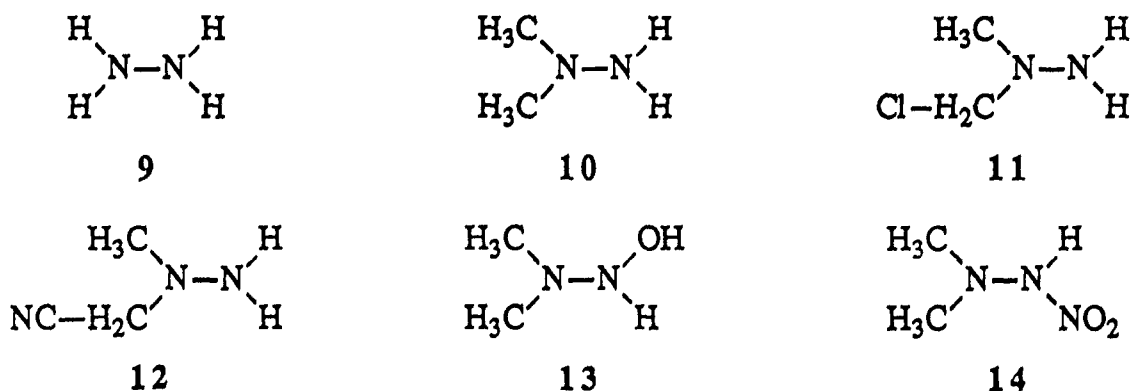
Our analysis showed that the most negative regions in these molecules (the sulfilimine intermediates as well as the original aminoazines) are associated with one or both of the ring nitrogens, rather than the exocyclic one that is to be oxidized. The key new feature in the case of 5 is the development of extensive negative regions above and below the ring plane, which make the exocyclic nitrogen much more accessible to electrophiles than it is in 4. Thus the likelihood of oxidation occurring at this site is considerably greater in 5 than in 4. The presence of the electron-withdrawing  $\text{NO}_2$  in 7 prevents the development of strong negative regions above and below the ring; accordingly there does not occur, in 8, an analogous increase in electrophilic accessibility to the exocyclic nitrogen, and indeed its oxidation is not observed.

We tested computationally whether the exocyclic sulfilimine nitrogen could be made more negative by decreasing the C-N-S angle, thereby possibly making the nitrogen lone pairs more concentrated. (In practice, this might be achieved by replacing one of the methyl groups by  $\text{CHCl}_2$ ; if this hydrogen-bonded to the nearest ring nitrogen, there could result a decrease in the C-N-S angle.) However when this idea was tested by forcing an arbitrary decrease in this angle, from  $106^\circ$  to  $100^\circ$ , the desired increase in negative character of the exocyclic nitrogen was not observed.

We also examined the possibility of using  $P(CH_3)_3$  rather than  $S(CH_3)_2$  to form the activated intermediate, to determine whether this might make the exocyclic nitrogen more reactive. On the contrary, however, we found that the phosphorus analogue of 5 does not have nearly as strong and extensive negative regions above and below the ring, so that the exocyclic nitrogen would be expected to be much less reactive.

#### D. Oxidation of Hydrazines

As a means of gaining insight into the reasons for the difficulties encountered in trying to oxidize hydrazines to the corresponding nitramines, we investigated hydrazine (9) and five of its derivatives (10 - 14) [18]. We have shown that an effective measure of the dihedral angle between the central nitrogen lone pairs can be obtained from the positions of the electrostatic potential minima in these regions. On the basis of our analysis, we feel that the problems associated with the controlled oxidation of hydrazines may reflect the fact that two factors which would favor this - highly negative nitrogen potentials and relatively strong N-N bonds - are opposing in nature.

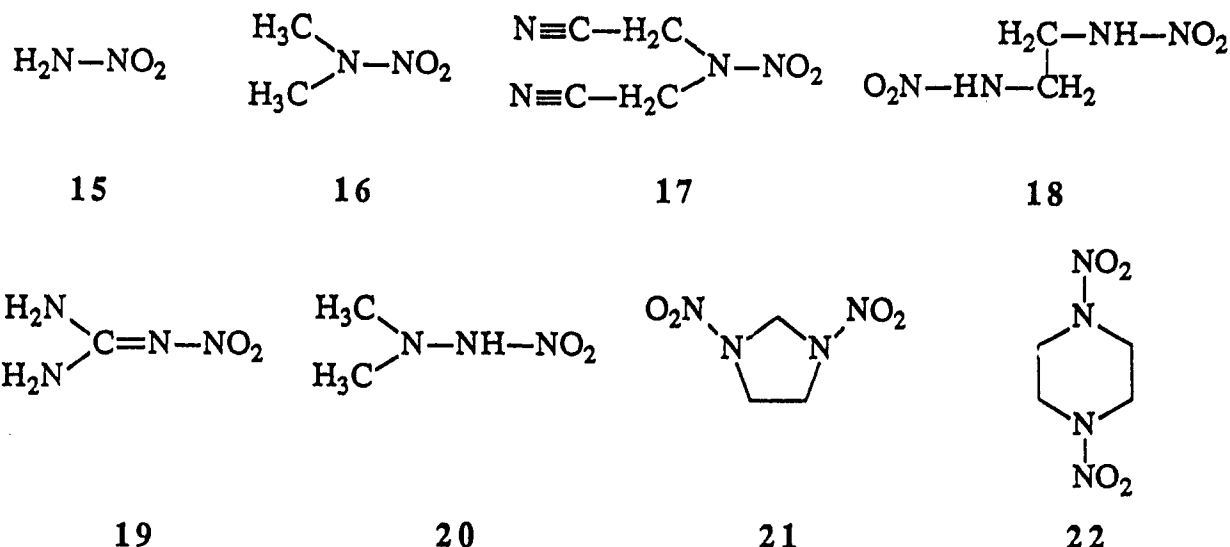


### IV. Fundamental Properties of Nitramines

#### A. Structural and Reactive Properties

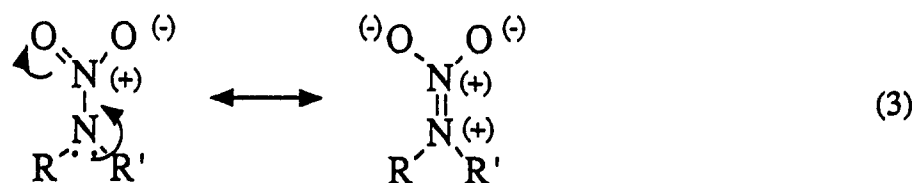
We carried out a computational study of six noncyclic nitramines,  $\begin{array}{c} R' \\ \diagdown \\ N-NO_2 \\ \diagup \\ R'' \end{array}$ , and

two alicyclic nitramines with the objective of better understanding how the properties of the  $N-NO_2$  group are affected by the natures of  $R'$  and  $R''$ , ring size and conformation. We calculated the optimized geometries, bond orders (as measures of bond strength), and electrostatic potentials of the noncyclic systems 15 - 20 [19], and the geometries and electrostatic potentials of 21 and 22 (as well as their unsubstituted parent imidazolidine and piperazine rings) [20].



The key portions of 16 - 19 were found to be planar, with a significant degree of double bond character in the N-NO<sub>2</sub> bond; the latter is weakest in 19 and 20. The planarity of the amine nitrogens in 16 - 19, reflecting in part the electron-withdrawing power of NO<sub>2</sub>, nearly eliminates the strong negative electrostatic potentials (and hence basicity) normally associated with the lone pairs of amine nitrogens. However the imine nitrogen in 19 and the pyramidal amine nitrogens in 20 do retain strong negative lone pair potentials. An interesting feature of the nitramines 15 - 18 is the presence of a significant hyperconjugative effect, resulting in enhanced acidic character.

Imidazolidine and its 1,3-dinitro derivative 21 have gas phase equilibrium geometries that are puckered, while the most stable conformers of the piperazines (e.g. 22) are chairs. The introduction of nitro groups results in a greater degree of ring flattening in 21 than in 22; resonance delocalization of the amine lone pair toward the nitro group, as shown in eq. (3), occurs to a higher



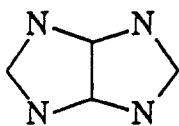
degree in the former, which has shorter N-N bond lengths and weaker negative potentials associated with its amine lone pairs.

### B. Anomalous Energetic Effects

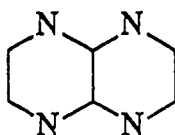
A very interesting and rather striking effect that we have discovered is that there is an anomalous stabilization associated with replacing carbons by aza nitrogens in aliphatic and alicyclic molecules, both strained and unstrained [20,21]. This finding is based upon calculated isodesmic

reaction energies. We attribute this stabilization to  $\sigma$ -conjugation of the nitrogen lone pairs. It increases with the number of nitrogens, and is greater for cyclic molecules, particularly when there are fused rings. N-nitro substitution to produce nitramines has an additional stabilizing effect, which may reflect further delocalization of  $\sigma$  electrons, particularly the amine lone pairs, due to the strongly electron-withdrawing nitro group. The recognition of these anomalous stabilizing tendencies helps to explain some heretofore puzzling observations, such as the unexpected stability of the imidazolidine framework that has been encountered in the thermal decomposition of 1,3-dinitroimidazolidine (21).

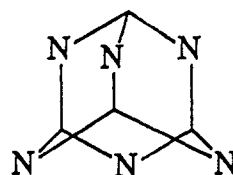
A potentially important aspect of aza nitrogen stabilization is that the 1,3-diaza combination is particularly favored, possibly because the  $\sigma$ -delocalization of one nitrogen lone pair can reinforce that of the other [21]. Thus the stabilization of both 23 and 24 is more than double that of the individual rings, because fusing the rings creates additional 1,3-diaza groupings. The effect is much greater for 23 than for 24, however, because the former contains four such combinations and the latter only two.



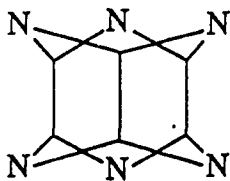
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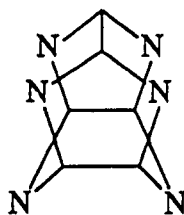
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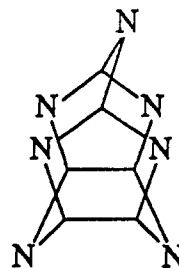
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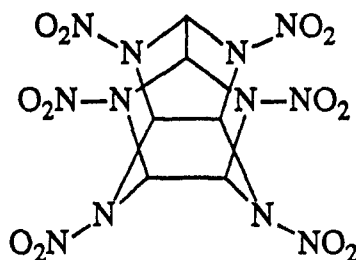
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In view of these findings, certain predictions can be made. For example, hexaazaadamantane, 25, should show enhanced stability, compared to both hexaazawurtzitane, 26 and 27, because 25 contains twelve 1,3-diaza groupings compared to six for each of the latter. However the introduction of an aza bridge in 27, to give 28, would add four more stabilizing 1,3-diaza combinations. All of these comments would pertain as well to the corresponding nitramines. In general, it can be anticipated that the stabilizing effects of aza nitrogens will be important both for facilitating syntheses and in diminishing the sensitivities of energetic molecules.

## V. Computational Analyses of CL-20 Polymorphs

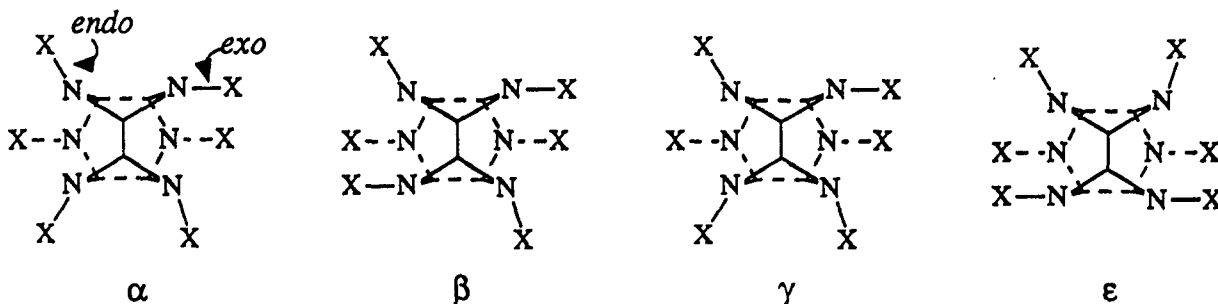
Our computational studies of CL-20 (29) have had several objectives [22-24]:

- to determine the relative impact and shock sensitivities of the four known polymorphs of 29;
- to gain insight into the possibility of forming clathrates with various small molecules (e.g. H<sub>2</sub>O, NH<sub>3</sub>, NH<sub>2</sub>OH, HN<sub>3</sub>, etc.), thereby potentially increasing energy content and/or decreasing sensitivity;
- to predict key properties of the suspected  $\delta$  and  $\zeta$  polymorphs.



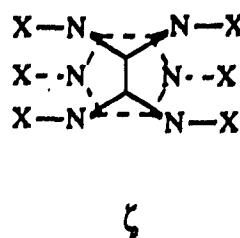
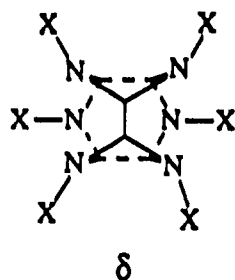
29 CL-20

The four known polymorphs of CL-20 can be distinguished through the differing orientations (*endo* or *exo*) of the NO<sub>2</sub> groups on the five-membered imidazolidine rings. This is shown below, following the format used by the Naval Weapons Center. (The  $\alpha$  and  $\gamma$  polymorphs are quite similar with regard to the orientations of these NO<sub>2</sub> groups.)



Top views of polymorphic forms; X = NO<sub>2</sub>

Crystallographically-determined structures of these four polymorphs were kindly provided to us by Dr. Richard Gilardi (Naval Research Laboratory). It has been suggested that two other polymorphic variations, designated as  $\delta$  and  $\zeta$ , which are presently unknown, may eventually be found.



### A. Structural Studies

CL-20 can be viewed as two linked 1,3-dinitroimidazolidines (21) fused to 1,4-dinitropiperazine (22). In order to see how these separate units are distorted in forming the CL-20 cage, and at what cost in energy, we compared the earlier optimized structures of 21 and 22 [20] to the forms that they assume in 29 [1]. The calculations were done at the *ab initio* SCF 3-21G level.

The major effects that we found were the following [22]:

- (a) In the equilibrium structure of 21, the NO<sub>2</sub> groups are both *exo*. Forcing one of them to be to *endo* lengthens its N-NO<sub>2</sub> bond by 0.04 Å and weakens it; the calculated bond order decreases by about 10%. (We verified this by computing the bond orders in β-CL-20.) Overall, the molecule is destabilized by 4.4 kcal/mole.
- (b) The equilibrium structure of 22 has a chair conformation. Forcing it into the boat form, as in CL-20, increases its energy by 10 kcal/mole.

Thus in the case of β-CL-20, for example, the combined destabilization due to these factors is about 19 kcal/mole.

Using the structures obtained from NRL, we have computed *ab initio* SCF STO-3G wave functions and total molecular energies for the conformations corresponding to the four CL-20 polymorphs [22]. The lowest energy, on a molecular level, is associated with the ε; the relative energies in kcal/mole, taking ε as the reference point, are: ε, 0; γ, 12.7; α, 24.3; β, 40.9. (The α energy is for the CL-20 molecule alone, not including the water of hydration present in the crystal.)

We completed additional calculations designed to provide some insight into how the relative stabilities of the δ and ζ conformers may compare to those of the other forms [24]. Starting with the conformations depicted above for δ and ζ, we carried out *ab initio* STO-3G geometry optimizations to determine their equilibrium (gas phase) molecular structures and energies. In order to permit meaningful comparisons, the same was done for the ε conformer, which we had found to be the most stable of the other four.

At the *ab initio* STO-3G level, the ζ structure is not found to exist in the gas phase; our attempt to optimize its structure caused it to rearrange to the δ form. This instability of the ζ conformation is consistent with Gilardi's view that there would be steric hindrance to having *exo*

NO<sub>2</sub> groups on the same (seven-membered ring) side of the molecule, as would occur twice in the  $\zeta$  form.

We did obtain optimized structures for the  $\epsilon$  and  $\delta$  conformers, and confirmed that these do correspond to energy minima (by verifying that they have no imaginary frequencies). The  $\delta$  form was found to be more stable than the  $\epsilon$ , by 12.5 kcal/mole.

It should be noted that this result pertains to single molecules having the  $\epsilon$  and  $\delta$  conformations; their geometries (bond lengths, bond angles, etc.) were determined by optimization, and accordingly represent their equilibrium gas phase structures. The relative stabilities obtained earlier (for the  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\epsilon$  conformations) are also for single molecules but having geometries corresponding to their structures in the crystalline form. Hence the two sets of results should not be combined; e.g. it should not be inferred that the  $\delta$  conformation is  $12.7 + 12.5 = 25.2$  kcal/mole more stable than the  $\gamma$ .

#### B. Aza and Nitro Stabilization

As discussed earlier in this report, we have consistently found the presence of aza nitrogens to have a marked stabilizing effect, upon both strained and unstrained aliphatic and alicyclic systems [20,21]; this is attributed to sigma delocalization of the nitrogen lone pairs. We have computed this stabilization at the 3-21G level for the unsubstituted hexaazaisowurtzitane framework of CL-20, and find it to be 44 kcal/mole [22]. This is consistent with the stabilization energies of imidazolidine (11 kcal/mole) and piperazine (boat, about 7 kcal/mole), taking into account the fact that combining these into hexaazaisowurtzitane creates four new 1,3-diaza linkages, which introduce an additional anomeric stabilization.

A further stabilizing effect arises from NO<sub>2</sub> groups, when substituted on nitrogens (i.e. in nitramines) [21] but not necessarily when on carbons. This presumably reflects enhanced delocalization of the aza lone pair, due to the electron-withdrawing power of the NO<sub>2</sub>. For example, the total aza plus nitro stabilization in 1,3-dinitroimidazolidine is 23 kcal/mole, compared to 11 kcal/mole for imidazolidine itself [22]. While we have not computed this effect for CL-20 (due to the CPU time and disk space requirements at the SCF/3-21G computational level), it is certainly expected to be present.

#### C. Electrostatic Potentials of CL-20 Polymorphs

In order to provide insight into the relative tendencies for clathrate formation, we computed the electrostatic potentials of the  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\epsilon$  conformations. These show that the most negative potentials are associated with the *exo* NO<sub>2</sub> groups, which are accordingly predicted to have the strongest hydrogen-bond-accepting tendencies [23].

We also found that the presence of two *endo* NO<sub>2</sub>'s on the same five-membered ring face (as occurs in  $\alpha$ -,  $\gamma$ - and  $\delta$ -CL-20) produces a distinct cleft in the molecular surface (Figure 1), in which there is a strongly positive electrostatic potential [22]. In contrast, an *exo,exo* face has no cleft and is only weakly positive; the *endo,exo* combination is intermediate. Both of these are shown in Figure 2. Thus, the *endo,endo* should be particularly favorable to interactions with negative species, such as an anion, an NO<sub>2</sub> group on a neighboring CL-20 molecule, or a small polar molecule (e.g. H<sub>2</sub>O, NH<sub>2</sub>OH, etc.). We confirmed computationally that a stable interaction can occur between an *endo,endo* region and the oxygen of a water molecule; a stabilizing energy of -6 kcal/mole was obtained when the oxygen was about 4 Å from the central portion of the five-membered-ring [22].

Figure 3 presents the molecular surface between the two dinitroimidazolidine faces, above what can be regarded as seven-membered rings. On one of these views, a distinct cleft is evident, but the only highly positive region is quite small.

#### D. Shock Sensitivities and Specific Impulse

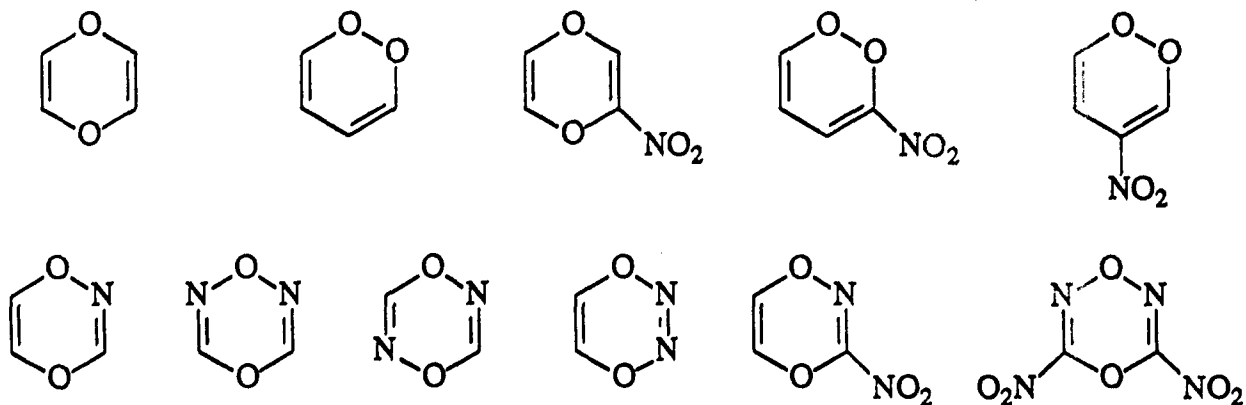
We have estimated the shock sensitivities of the CL-20 polymorphs, using the correlation that we have developed [3], and which was discussed in section I-B. The shock sensitivities of the four polymorphs are predicted to be very similar to each other, and to that of RDX [22].

We have computed the specific impulse for  $\beta$ -CL-20, using the program obtained from the Naval Weapons Center and also the one that we have written ourselves [1] (described in section I-A). By both approaches, we find the specific impulse to be about 4% greater than that of HMX [22].

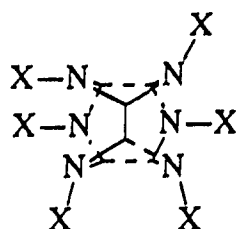
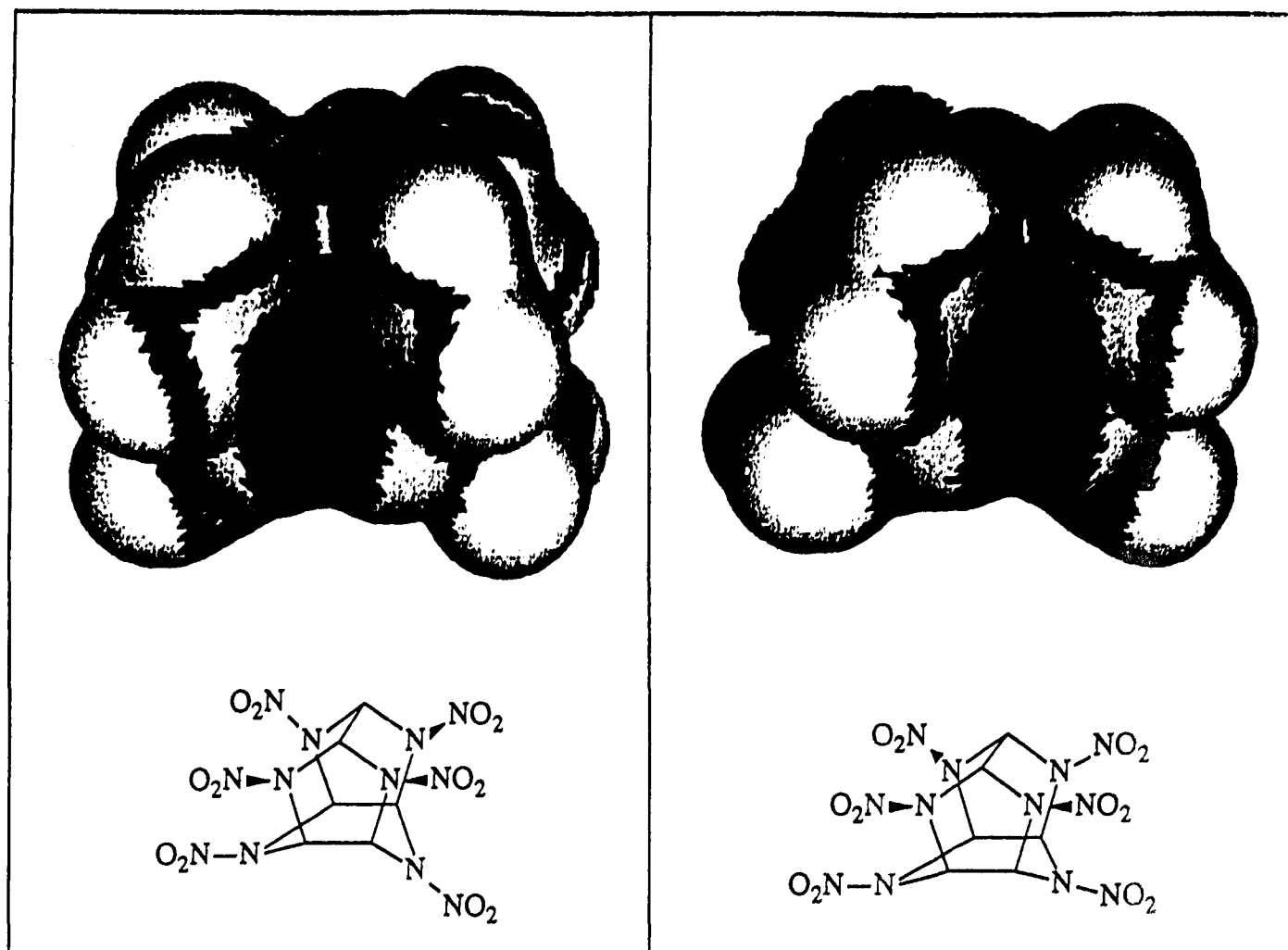
## VI. New Energetic Materials

### A. Heterocyclic Systems

We carried out extensive studies of unsaturated heterocyclic molecules and their nitro derivatives [25-28], shown below, which are of interest either as precursors to high energy

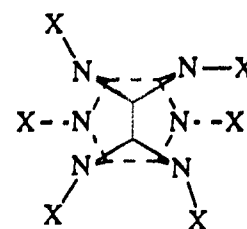


# SURFACE ELECTROSTATIC POTENTIALS



$V(r)$  ranges (kcal/mole):

BLUE: More positive than 40.  
 YELLOW: Between 20 and 40.  
 PURPLE: Between 0 and 20.  
 WHITE: Negative.

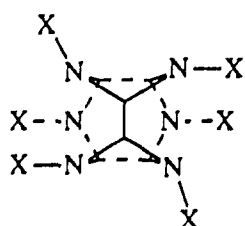
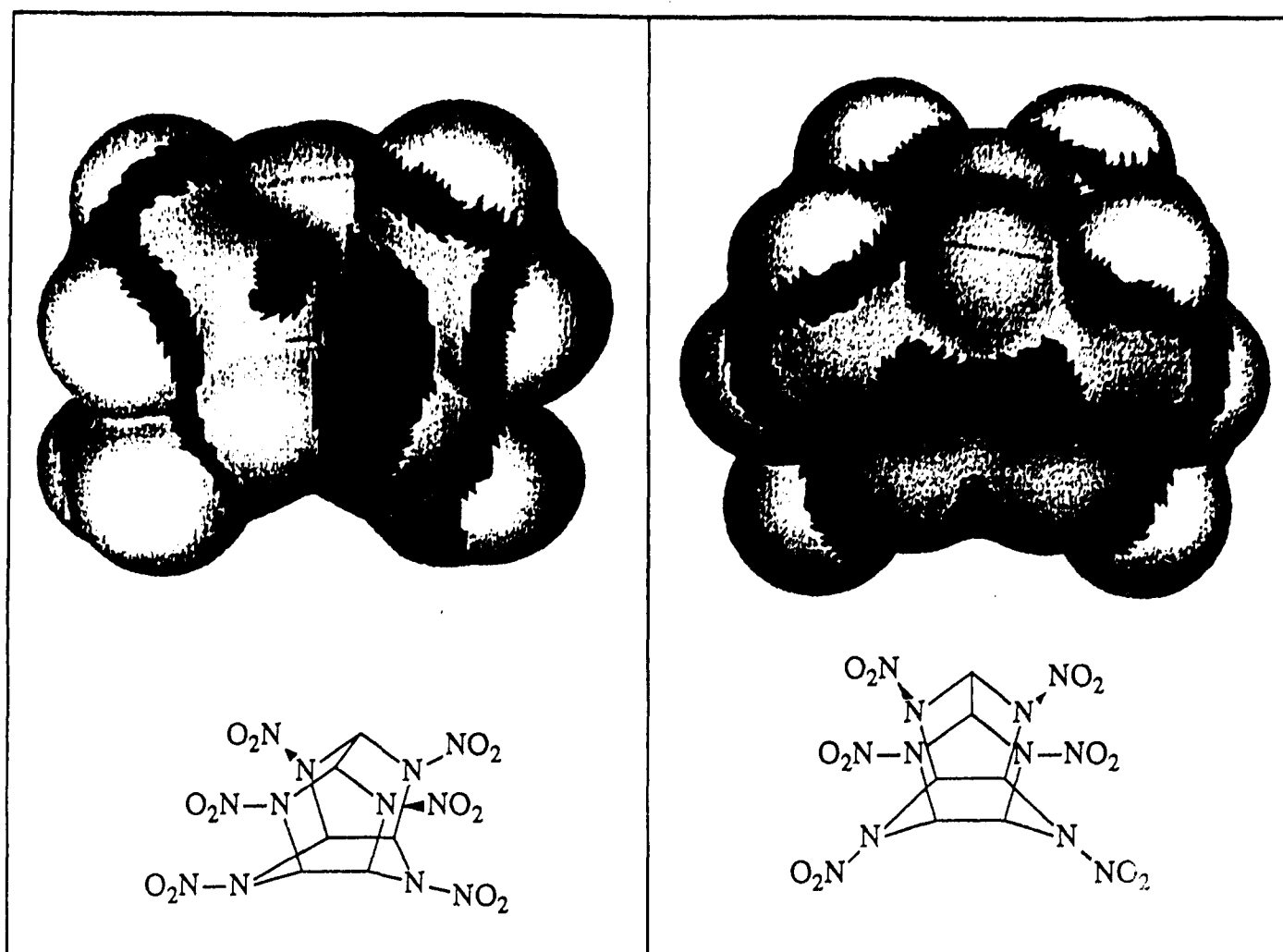


## OBSERVATIONS:

1. The two *endo*  $\text{NO}_2$ 's on the faces of the  $\alpha$  and  $\gamma$  polymorphs shown above produce a distinct cleft in the molecular surface in which there is a strongly positive (blue) electrostatic potential.
2. These strongly positive regions extend to the bottom of the molecular surfaces (associated with the six-membered rings). There are also blue areas at the top, over the C-C bonds.
3. These positive regions are favorable sites for interactions with negative species, such as an anion, an  $\text{NO}_2$  group on a neighboring CL-20 molecule, or a small polar molecule (e.g.  $\text{H}_2\text{O}$ ,  $\text{NH}_2\text{OH}$ , etc.)

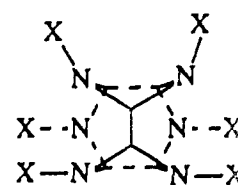
Figure 1.

# SURFACE ELECTROSTATIC POTENTIALS



$V(r)$  ranges (kcal/mole):

BLUE: More positive than 40.  
 YELLOW: Between 20 and 40.  
 PURPLE: Between 0 and 20.  
 WHITE: Negative.

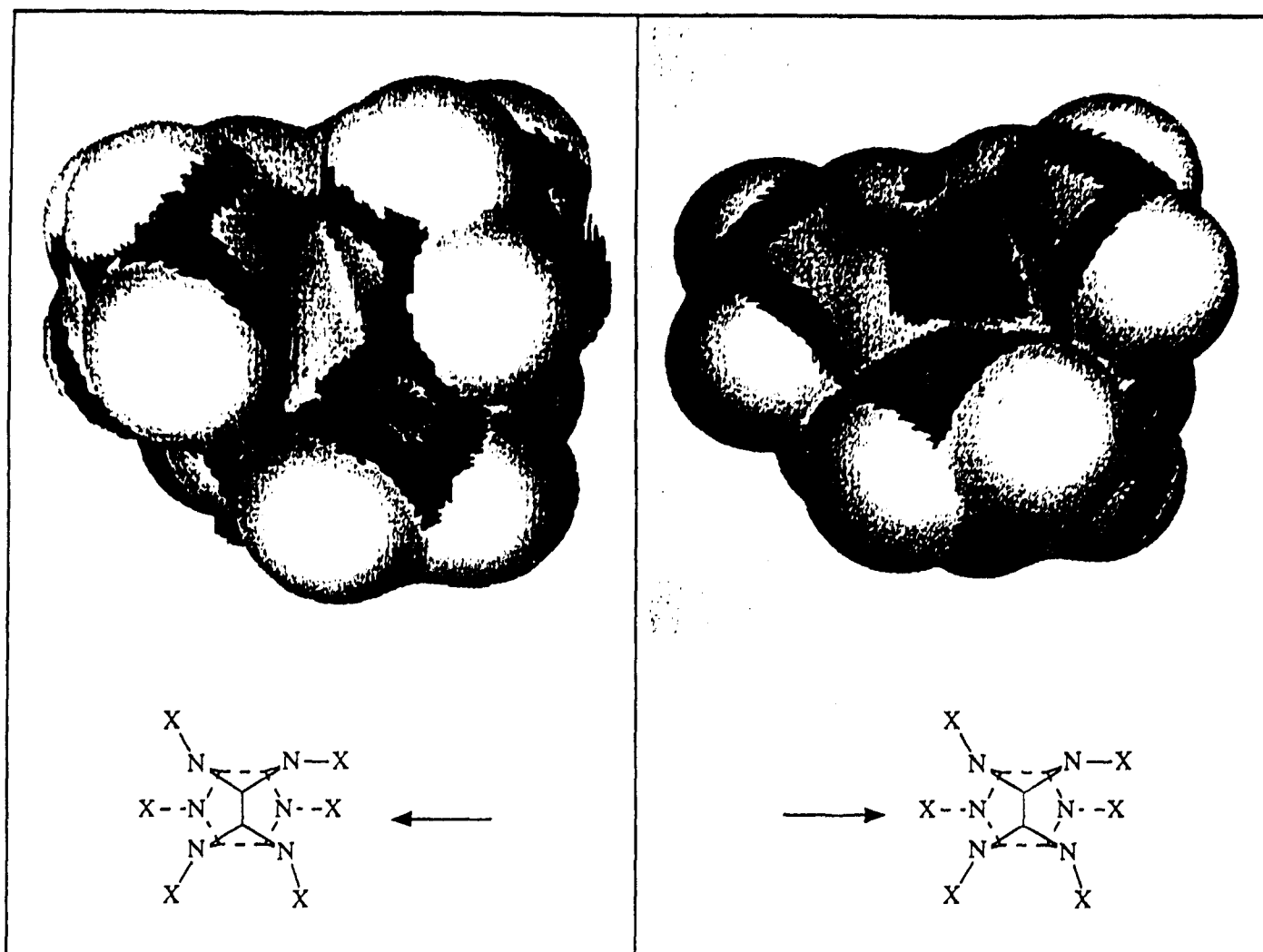


## OBSERVATIONS:

1. The presence of one *endo*  $\text{NO}_2$  in  $\beta$ -CL-20 (above left) has an effect analogous to that of two, but to a lesser degree; the highly positive region is only on the side by the *endo*  $\text{NO}_2$ .
2. The *exo, exo* face of  $\epsilon$ -CL-20 (above right) has no cleft and is only weakly positive (purple).

Figure 2.

# SURFACE ELECTROSTATIC POTENTIALS



## SIDE VIEWS OF $\gamma$ -POLYMORPH

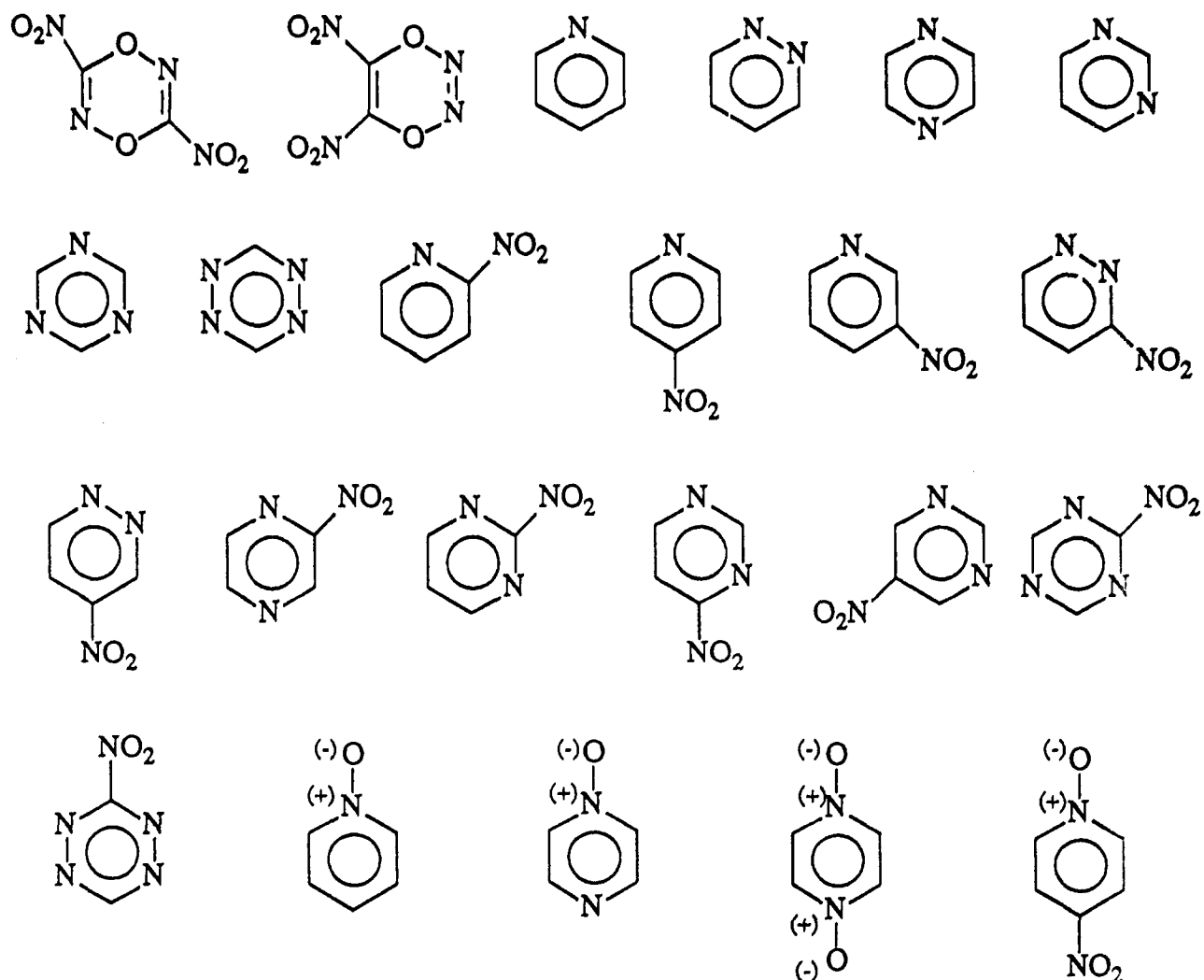
$V(r)$  ranges (kcal/mole):

BLUE: More positive than 40.  
 YELLOW: Between 20 and 40.  
 PURPLE: Between 0 and 20.  
 WHITE: Negative.

### OBSERVATIONS:

1. The side views of  $\gamma$ -CL-20 examine the molecular surfaces between the two dinitroimidazolidine faces, facing what can be regarded as seven-membered rings.
2. A distinct cleft is seen in the view with one *endo* and one *exo* NO<sub>2</sub> (above left); its only highly positive region however is quite small.
3. The central portion of the view with two *endo* NO<sub>2</sub>'s (above right) is relatively flat and only weakly positive.

Figure 3.



systems or as target molecules themselves. Our analyses have focused on their structural features, relative stabilities and reactive behavior.

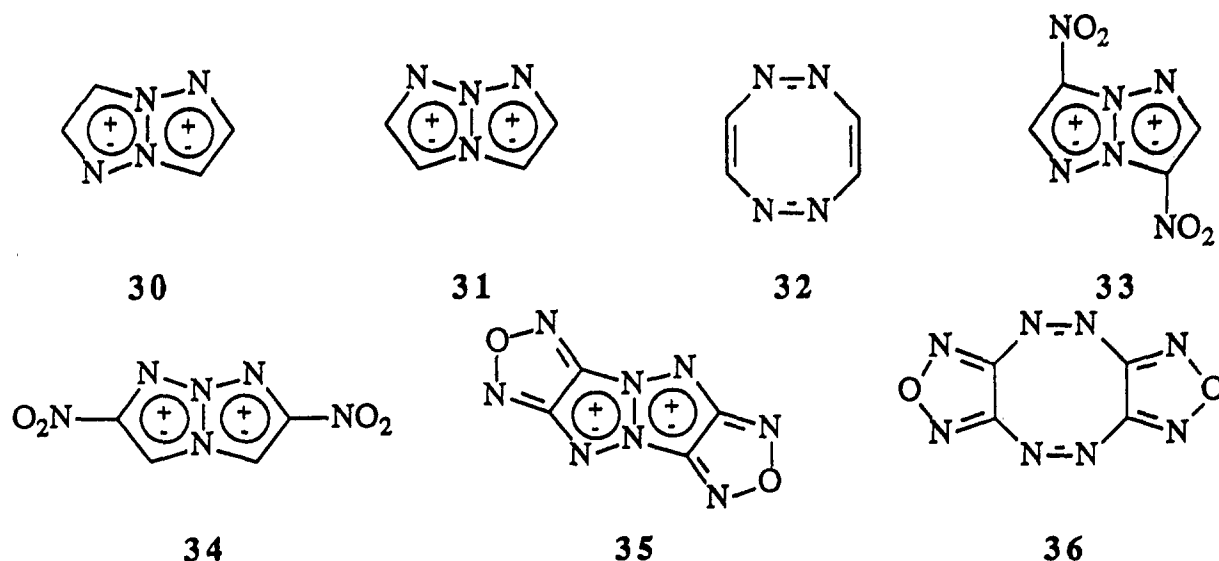
Among the various dioxins, dioxadiazines and azines, we invariably found that those having two adjacent ring oxygens or nitrogens were the least stable [25]. Within the nitroazines, the energetically preferred site for the  $\text{NO}_2$  substituent is a carbon  $\beta$  to a ring nitrogen, while the  $\alpha$  position is the most unstable.

The electrostatic potentials of the unsubstituted systems are dominated by relatively strong negative regions associated with the ring nitrogens and oxygens, indicative of basic character; there are also weak negative potentials above the C-C double bonds in the dioxins and dioxazine and above the aromatic region of pyridine [27,28]. Introduction of  $\text{NO}_2$  weakens the negative potentials of the ring heteroatoms, and completely eliminates those above the double bonds and aromatic rings. All of the nitro and N-oxide derivatives show buildups of positive potential above

the rings, suggesting susceptibility to nucleophilic attack [25-28]. The charge donor role of the N-oxide group allows the aromatic ring in pyridine N-oxide to be susceptible to electrophiles (at the *para* position) as well as nucleophiles [28].

### B. Tetraazapentalenes

Since certain tetraazapentalenes are known or predicted to have desirable properties (with respect to explosive and/or propellant performance), we have computed structures, relative stabilities and electrostatic potentials for the unsubstituted systems 30 and 31, the isomer 32, and the dinitro and difurazan derivatives 33 - 36 [29].

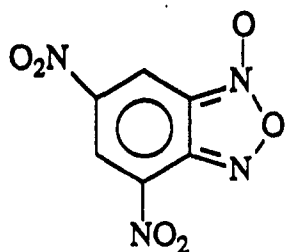


We find 30 and 31 to have high degrees of electron delocalization, and to be much more stable than 32, which has localized double bonds. However 35 and 36 show a reversal of these relative stabilities. There are strong negative electrostatic potentials, indicative of basic character, associated with the doubly-coordinated nitrogens in all of these molecules; these become weaker as other portions of the system become more electron-withdrawing. There is a buildup of positive potential above the bond between the triply-coordinated bridgehead nitrogens in 30 and 31. This region should accordingly be an attractive initial site for nucleophilic attack. The positive buildup becomes progressively stronger in going to 33 and 35. We estimate the specific impulse of 35 to be 42% better than that of HMX, that of 36 to be 18% better, and 33, 15% better.

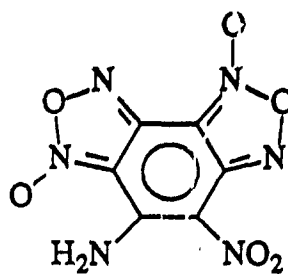
### C. Benzofuroxans and Furoxans

In response to interest expressed by Dr. May Lee Chan and Dr. Charlotte K. Lowe-Ma (Naval Weapons Center, China Lake), we carried out a computational analysis of the benzo-

furoxans 37 and 38 [30]. We calculated atomic charges, ionization energies and dipole moments, and also presented some preliminary comments concerning their impact/shock sensitivities.

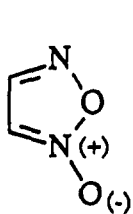


37



38

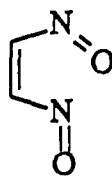
We have investigated the structural properties and relative stabilities of furoxan (39) and some of its isomers (40-46) by means of *ab initio* Hartree-Fock and Møller-Plesset calculations [31]. Some of these systems are models for decomposition products of furoxan-type materials (e.g. benzofuroxan, 47). Furoxan was found to be the most stable of these isomers at all computational levels. The results of our calculations were markedly affected by electronic correlation, which renders 44 - 46 unstable. It also emphasizes the importance of a zwitterionic contribution to the structure of furoxan. We examined the ring-opening transition from 39 to 40/41, which proceeds through a *cis*-1,2-dinitrosoethylene-like intermediate/transition state.



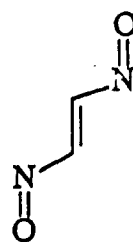
39



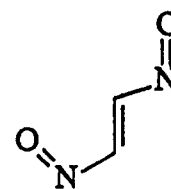
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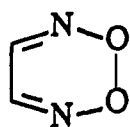
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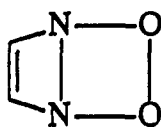
42



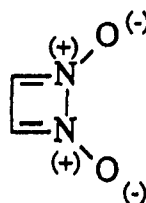
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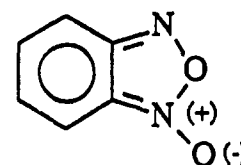
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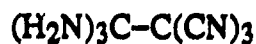
47

#### D. Highly Polar or Ionic C-C Bonds

As part of a study of systems containing highly polar or ionic C-C bonds, we computed structures and properties for 48 and 49,

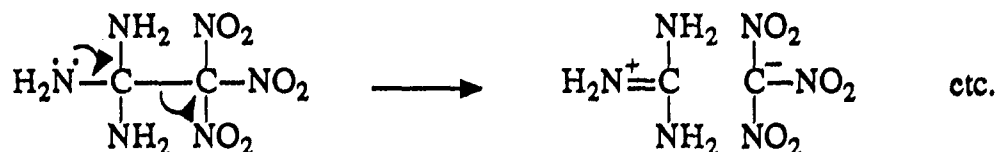


48



49

and for the ions:  $^+\text{C}(\text{NH}_2)_3$ ,  $^-\text{C}(\text{NO}_2)_3$ ,  $^-\text{C}(\text{CN})_3$  and  $^-\text{C}(\text{NO}_2)_2\text{CN}$  [32]. This work was done in collaboration with Dr. J. H. Boyer (University of New Orleans), who has synthesized 48. We find the C-C bonds in 48 and 49 to be unusually long, 1.60 Å, compared to the typical value of 1.53 Å. This is consistent with contributions from ionic structures:

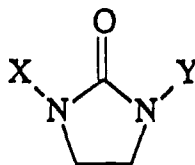


The other calculated bond lengths also fit this picture. The computed heterolysis energies for the C-C bonds in 48 and 49 are 59 and 63 kcal/mole, respectively, compared to 342 for ethane. 49 is a possible precursor to a trinitromethyl derivative of hexazaadamantane (25).

#### E. Difluoramino and Related Systems

Due to the interest in the propellant qualities of energetic difluoramino derivatives, we have determined some of the properties associated with the  $\text{NF}_2$ ,  $\text{NF}$  and  $\text{NHF}$  groups. We have computed the specific impulses for more than 30 molecules containing these groups, and find generally significant improvement over the nitro analogues [2]. This reflects fluorine's more efficient use of whatever hydrogen is present, since each fluorine requires only one hydrogen to yield a gaseous product ( $\text{HF}$ ), whereas each oxygen needs two (for  $\text{H}_2\text{O}$ ). Isodesmic reaction analyses show that the  $\text{NF}_2$  group stabilizes a molecule thermodynamically. We have used our correlation between local ionization energies on molecular surfaces and substituent constants to predict the latter for  $\text{NF}_2$  and  $\text{NHF}$  [33]. [ $\text{NF}_2$ :  $\sigma_p = 0.49$ ,  $\sigma_m = 0.54$ ,  $\sigma_I = 0.53$ ,  $\sigma_R = -0.04$ ;  $\text{NHF}$ :  $\sigma_p = 0.06$ ,  $\sigma_I = 0.43$ ,  $\sigma_R = -0.37$ .] Finally, we have shown by means of surface electrostatic potentials that while the  $\text{NF}_2$  group does sensitize cyclic ureides (e.g. 50) toward hydrolysis, the effect is considerably less than that of  $\text{NO}_2$  [34].

X, Y =  $\text{NO}_2$ ,  $\text{NF}_2$ , H



50

## F. Dinitramide Anion, $N(NO_2)_2^-$ , and Related Molecules

Recent synthetic work by Schmitt and Bottaro has focused attention upon potential energetic systems involving the dinitramide ion,  $N(NO_2)_2^-$ . We have accordingly computed the structures of  $N(NO_2)_2^-$  and some related molecules:  $HN(NO_2)_2$  and  $N(NO_2)_3$ . We analyzed factors affecting their stabilities, and computed the proton affinity of  $N(NO_2)_2^-$  (as a measure of the acidity of  $HN(NO_2)_2$ ) and the interaction energy of  $N(NO_2)_2^-$  with  $NO_2^+$  to yield  $N(NO_2)_3$  [35]. The proton affinity of  $N(NO_2)_2^-$  was found to be considerably greater than that of  $NO_2^-$ . (For our prediction of the aqueous  $pK_a$  of  $HN(NO_2)_2$ , see section VII-B.)

## G. Strained Hydrocarbons and Their Derivatives

### 1. *General Properties:*

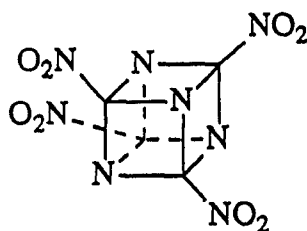
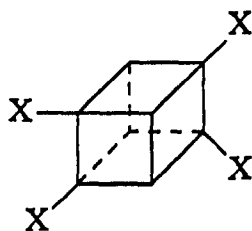
We have analyzed and compared fourteen different strained hydrocarbons and a variety of their derivatives, involving such substituents as  $NO_2$ ,  $NO$ ,  $CF_3$ ,  $NH_2$ ,  $NCO$ , etc. Our analysis was in terms of the bond deviation index, which is a measure of the degree of bending (and strain) associated with a bond, and the electrostatic potential [36]. There are consistently negative potentials near the midpoints of the C-C bonds in strained hydrocarbons (but not necessarily their derivatives), although there is no correlation between the magnitudes of these potentials and the corresponding bond deviation indices. It is interesting to note also that the degree of bond bending is not directly related to the amount of electronic charge in the bond region.

We have shown that the bond deviation index is an effective means for assessing the validity of treating a larger strained hydrocarbon as composed of fused or linked smaller ones. We also find that the degree of strain in C-C bonds depends much more upon the parent hydrocarbon than upon the natures of any substituents. Electrostatic potentials, on the other hand, are usually dominated by the negative regions associated with the substituents themselves; the weaker C-C bond potentials of the original hydrocarbons are often considerably modified or even absent in the substituted systems, although the bonds do remain bent.

### 2. *Cubanes and Azacubanes:*

There continues to be considerable interest in cubane-type systems as energetic materials. Since  $NH_2$  as well as  $NO_2$  is a possible substituent, whether in the target molecule or a precursor, and in view of the well-known weakening of a strained C-C bond linking carbons that simultaneously bear  $NH_2$  and  $NO_2$  groups, we have studied in detail the effects of these groups -- singly or together -- upon the C-C and C-N bonds in cubane and some azacubanes [37,38]. The latter were included because of the stabilization that we consistently find to be associated with aza

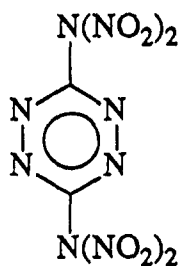
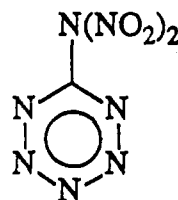
nitrogens [21], and because our calculations also show them to improve energetic performance (e.g. specific impulse [2]). We find that  $\text{NO}_2$  may strengthen or weaken several C-C bonds, depending upon its conformation, whereas  $\text{NH}_2$  weakens one specific bond, determined by the orientation of the amine lone pair. These effects of  $\text{NO}_2$  and  $\text{NH}_2$  are essentially independent of each other; when the groups are on adjacent carbons, these separate tendencies reinforce each other. Aza nitrogens were found to diminish these bond weakening effects, leading to our suggestion that 1,3,5,7-tetra-nitrotetraazacubane, **51**, is particularly promising as an energetic system from the standpoints of both a high level of performance and also feasibility of synthesis [37].

**51****52**

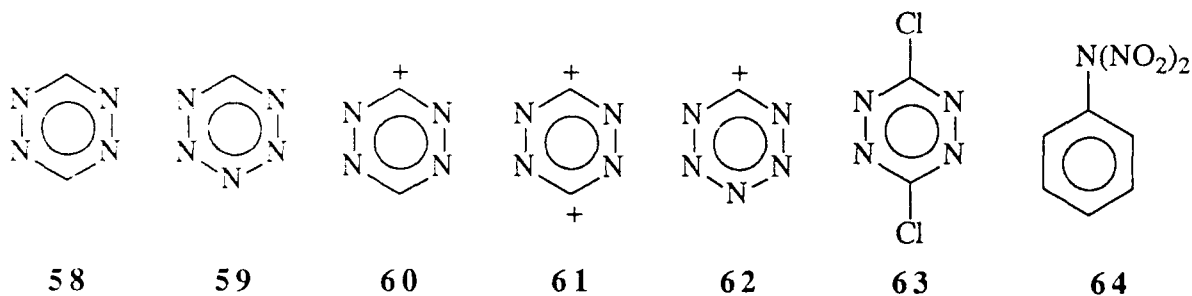
Dr. R. L. Willer sent us the crystal structure of **52**, the tetra-N-nitromethylcarbamate of cubane, and asked that we calculate the C-C bond orders by our technique, which requires first computing the vibration frequencies. We found the bonds between the substituted carbons to be the weakest, weaker also than in cubane itself.

#### H. Dinitramine Derivatives of Polyazines (suggested by Dr. R. S. Miller)

We have carried out an investigation of the structures, stabilities and reactive behavior of **56** and **57**. Since one of the key questions concerns the possibility that **56** and **57** may exist as

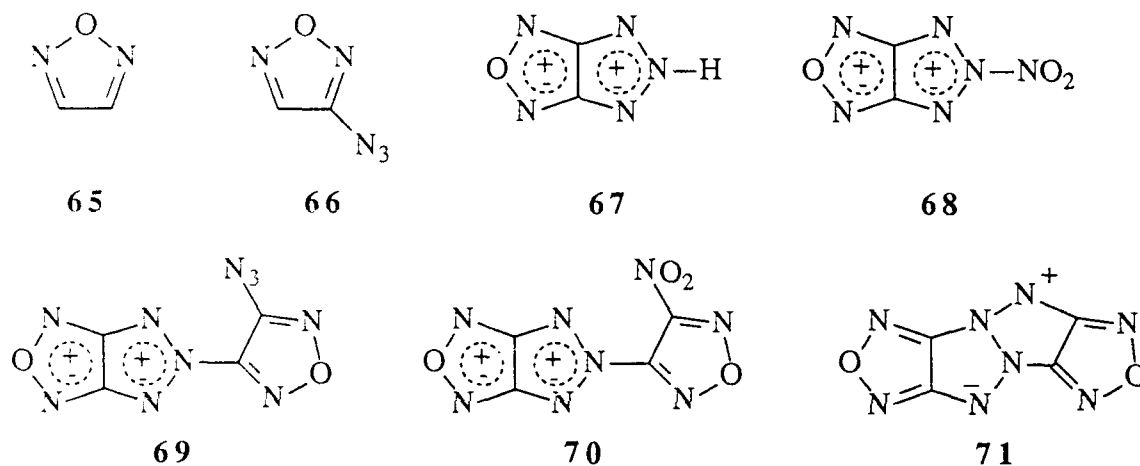
**56****57**

ionic compounds, our study has encompassed both the neutral and cationic forms of the parent systems, **58** - **62**, as well as the related molecules **63** and **64**; the latter was included in order to determine the Hammett constants of the  $\text{N}(\text{NO}_2)_2$  group [39]. These were found to be:  $\sigma_m = 0.87$ ;  $\sigma_p = 0.73$ .



### I. Mesoionic Bicyclic Systems

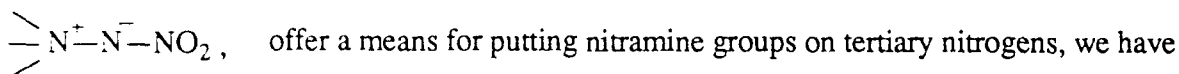
Complementing synthetic work by Dr. J. H. Boyer, we have carried out a computational study of the furazans **65** and **66** and the mesoionic bicyclic systems **67** - **71** [40].



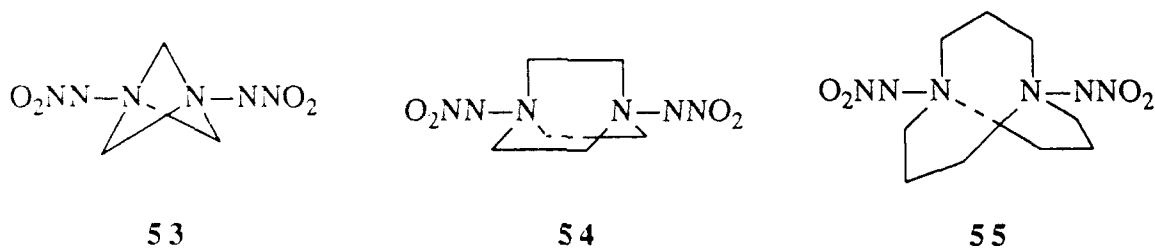
**69** could, in principle, be a precursor to either **70** or (by elimination of  $N_2$ ) **71**.

### J. Zwitterionic N-Nitroimide Systems

Following upon Olah's interesting suggestion that zwitterionic N-nitroimides,



studied the properties of **53** - **55**, as well as the unsubstituted parent diazapropanes. (**54** has already been prepared by Olah.). We have computed structures, relative bond strengths, strain



energies and electrostatic potentials, with the aim of determining the stabilities and reactive properties of these molecules [41]. The unsubstituted parent of **55** has the interesting feature of a region of negative potential between the nitrogens, in the interior of the molecule. At Olah's request, we have also computed  $\Delta E$  for reaction (4):



Using SCF 3-21G optimized geometries, but computing the energies with the local density functional procedure, we found  $\Delta E = -66$  kcal/mole.

## VII. Molecular Reactive Properties

Two of our key computational tools in analyzing and predicting molecular reactive behavior are the electrostatic potential,  $V(\mathbf{r})$  [42-44], and the average local ionization energy,  $\bar{I}(\mathbf{r})$  [45]. Since we are increasingly using local density functional (LDF) theory in studying large molecules, one of our recent objectives has been to determine how reliable it is for calculating  $V(\mathbf{r})$  and  $\bar{I}(\mathbf{r})$ . We have now established that the LDF approach is effective for the former [46,47], and are currently investigating its applicability to  $\bar{I}(\mathbf{r})$ .

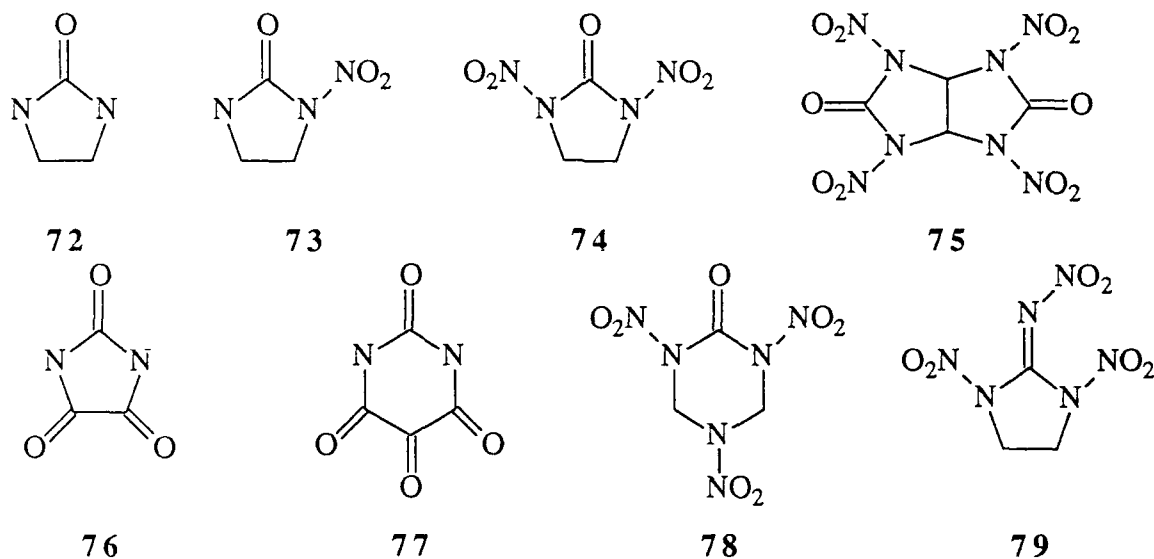
We have introduced the concept of computing  $V(\mathbf{r})$  and  $\bar{I}(\mathbf{r})$  upon three-dimensional surfaces encompassing molecules of interest [33,42,45,48]. These are defined individually and uniquely for each molecule in terms of its electronic density function. Other properties that we can now calculate on these surfaces are electric fields and spin densities. Surface  $\bar{I}(\mathbf{r})$  and  $V(\mathbf{r})$  have both been shown to be very effective in identifying sites for electrophilic attack and in ordering their relative reactivities [33,42-45], while the surface electrostatic potential is uniquely well suited for identifying regions susceptible to nucleophilic attack [34,42-44,48], as will be discussed below.

### A. Nucleophilic Processes

A particular benefit of the molecular surface approach has been in interpreting and predicting nucleophilic processes. In the past, these could not readily be treated by means of the electrostatic potential because the effects of the nuclei are so strong that they often mask local maxima that would indicate sites for nucleophilic attack. However the molecular surface is sufficiently removed from the positions of the nuclei that this problem is avoided. We have demonstrated that the regions of positive electrostatic potential on the molecular surface do reveal and rank the sites most susceptible to interaction with nucleophiles [34,42-44,48].

A very important application of this procedure is in analyzing and predicting the stabilities of energetic molecules toward hydrolysis, in which water acts as a nucleophile. For example, our

calculations have brought out the increasing susceptibility to hydrolysis of the acyl carbons in the series **72** - **74**, culminating in **75** ("Sorguyl"), known to be highly unstable toward hydrolysis [34,42]. In addition to the difluoramino compounds mentioned elsewhere in this report (**50**), we have also analyzed the relative susceptibilities to hydrolysis of **76** and **77** [34], and **78** and **79** [49]; the latter two are existing energetic compounds.



#### B. Correlations with Experimentally-Determined Indices of Reactivity

In addition to using  $V(r)$  and  $\bar{I}(r)$  for identifying and ranking sites for electrophilic and nucleophilic attack, we have recently shown that they correlate well with a number of other key indices of reactivity. In the past, these latter normally had to be determined experimentally; now we can accurately predict their values computationally, as summarized below.

$\bar{I}(r)$  can be used to predict:

- (a) Aqueous acidity,  $pK_a$  [45,50].
- (b) Hammett substituent constants:  $\sigma_m$ ,  $\sigma_p^\circ$  and  $\sigma_p$  [33].
- (c) Taft inductive substituent constant,  $\sigma_I$  [45].

$V(r)$  can be used to predict:

- (a) Hydrogen-bond-donor parameter,  $\alpha$  [51].
- (b) Hydrogen-bond-acceptor-parameter,  $\beta$  [52].
- (c) Taft substituent constants,  $\sigma_I$  and  $\sigma_I + \sigma_R$  (when  $\sigma_R > 0$ ) [42,44].

It is important to note that these are *solution* properties for which we now have computational predictive capabilities. Thus, for example, we predict the aqueous  $pK_a$  of  $HN(NO_2)_2$  to be -5.6.

VIII. References

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# INDEX OF RESEARCH PUBLICATIONS RESULTING FROM CONTRACT WITH OFFICE OF NAVAL RESEARCH

Contract No. N00014-85-K-0217 (0069)

## Articles in print:

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- (32) "A Computational Study of the Concerted Triple Dissociations of 1,3,5-Triazacyclohexane and Its 1,3,5-Trinitro Derivative (RDX)."  
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Articles accepted for publication and in press:

- (33) "Chemical Applications of Molecular Electrostatic Potentials"  
P. Politzer and J. S. Murray,  
*Trans. Amer. Cryst. Assoc.*, Vol. 26, in press.
- (34) "Effect of the Amine Group on Relative Bond Strengths in Cubane and Azacubanes"  
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- (37) "Correlations Between Molecular Electrostatic Potentials and Some Experimentally-Based Indices of Reactivity"  
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- (40) "C-H Bond Dissociation of Acetylene: Local Density Functional Calculations"  
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- (41) "Computational Analyses of CL-20 Polymorphs"  
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- (42) "Calculated Structures and Relative Stabilities of Furoxan, Some 1,2-Dinitroso-  
ethylenes and Other Isomers"  
J. M. Seminario, M. Concha and P. Politzer, J. Comput. Chem., in press.

Articles submitted for publication:

- (43) "An Analysis of Molecular Electrostatic Potentials Obtained by a Local Density  
Functional Approach"  
J. S. Murray, J. M. Seminario, M. C. Concha and P. Politzer,  
Int. J. Quantum Chem., submitted.
- (44) "Some Applications of Local Density Functional Theory to the Calculation of  
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- (24) "Computational Analysis of Some Possible Initial Steps in the Unimolecular Thermal Decompositions of 1,3-Diazacyclobutane and its 1,3-Dinitramine Derivative"  
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